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Application of first and second order biodegradation rate kinetic model on remediation of crude oil polluted soil environment

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To Cite:
Philip UE, Adianimovie S. Application of first and second order biodegradation rate kinetic model on remediation of crude oil polluted soil environment. *Discovery* 2023; 59: e71d1266

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Peer-Review History
Received: 20 March 2023
Reviewed & Revised: 24/March/2023 to 09/May/2023
Accepted: 13 May 2023
Published: June 2023

Peer-Review Model
External peer-review was done through double-blind method.

Discovery
pISSN 2278–5469; eISSN 2278–5450

ABSTRACT
This research deals on the application of first and second order biodegradation rate kinetic model on remediation of crude oil polluted soil environment. Experiments were made on swampy and clay soil environment using moringa seed shell and elephant grass which was grounded into powdered form as remediants and later compared with NPK fertilizer and yeast as part of the bioremediation process. The obtained results were used to determine the maximum specific rates, dissociation constant as well as the kinetic values in terms of first and second order kinetic. The behaviour of TBC and TPH in clay soil were similar to swampy soil. In the model evaluation, the correlation coefficient values (R^2) obtained from the Michalis-Menten model were higher compared to first and second order degradation rate models. Thus, the ranges of R^2 value obtained from the predictive models are 0.9053 to 0.9794 for first order degradation rate, 0.7904 to 0.8796 for second order degradation rate and 0.8839 to 0.9979 for Michalis-Menten Equation. Hence, the Michalis-Menten Equation predicted the residual TPH better than the first and second order degradation rate models. However, the models are capable of predicting TPHs content in soil amended with moringa seed shell in powdered form, yeast and NPK in swampy soil (*moringa oleifera*) and elephant grass in powdered form, yeast and NPK in swampy soil (*pennisetum purpureum*) during bioremediation process.

Keywords: Bioremediation, degradation, pollution, environment, model, first and second order

1. INTRODUCTION
The feasibility of bioremediation depends on the location of contaminants. Approaches for implementation of bioremediation depend on whether the impacted soil to be treated is intact in the environment or it can be excavated for treatment in an offsite facility. If on site, the term in-situ remediation suffices and if off-site, it is described as ex-situ (Angelucci et al., 2017; Dorado et al., 2015). The term bioremediation has been made of two parts: "bios" means life and refers to living organisms and "to remediate" means to solve a problem.

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Bioremediation can also be described as a biological method used for the removal of contaminants from infected or polluted environment (Mapscarta, 2020). A point to emphasize here is that bioremediation and biodegradation should not be confused with each other. However, in this research, we tend to research on other biological methods possible for bioremediation, hence we adopted the use of moringa seed shell, NPK fertilizer and the application of First and Second Order Biodegradation Rate Kinetic Model for a better and effect bioremediation process (Nwankwegu et al., 2016; Patel and Kumar, 2016; Pino-Herrera et al., 2017; Talha et al., 2018).

2. METHODOLOGY

The First Order Biodegradation Rate Kinetic Model

The first order biodegradation rate kinetic model for prediction of TPH reduction was developed using the principle of mass conservation in a batch reactor. A typical batch reactor (Figure 1).

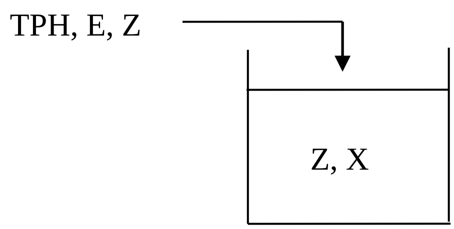

Figure 1 Batch Reactor

The principle of mass conservation is stated as

$$\left\{\begin{matrix}\text{Inflow of}\\ \text{mass into}\\ \text{system}\end{matrix}\right\} = \left\{\begin{matrix}\text{Outflow of}\\ \text{mass from}\\ \text{system}\end{matrix}\right\} + \left\{\begin{matrix}\text{Rate of}\\ \text{degradation}\\ \text{due to}\\ \text{reaction}\end{matrix}\right\} + \left\{\begin{matrix}\text{Rate of}\\ \text{accumulation}\\ \text{of mass}\\ \text{within system}\end{matrix}\right\} \qquad (1)$$

The degradation reaction that takes place in the reactor can be represented by equation (2).

$$TPH + E + Z \xrightarrow{k_s} P + E + Z \qquad (2)$$

Where;

TPH = Total hydrocarbon (pollutant) (g)

E = Bacteria

Z = Soil (kg)

P = Products

k_d = Degradation rate constant (unit according to model used)

From equation (1) we have

Inflow of mass into system $= Q_o C_{TPH(o)}$ (3)

Outflow of mass from system $= QC_{TPH}$ (4)

Rate of TPH degradation $= -r_{TPH} V$ (5)

Rate of accumulation $= -\dfrac{d(C_{TPH}V)}{dt}$ (6)

Substituting equation (3) through (6) gives

$$Q_o C_{TPH(o)} = QC_{TPH} - r_{TPH} V + \frac{d(C_{TPH}V)}{dt} \qquad (7)$$

Since there is no flow of materials in a batch reactor, the inflow of mass into reactor is equivalent to the out flow of mass from reactor.

Thus,

$$Q_o C_{TPH(o)} = QC_{TPH} = 0 \tag{8}$$

Also, for a batch process, volume of reactor (vessel) is constant hence, the accumulation term is

$$\frac{d(C_{TPH}V)}{dt} = V\frac{dC_{TPH}}{dt} \tag{9}$$

Therefore, equation reduces to

$$-r_{TPH}V = -V\frac{dC_{TPH}}{dt}$$

Or $$-r_{TPH} = -\frac{dC_{TPH}}{dt} \tag{10}$$

Assuming that the degradation of TPH is described by first order kinetics, then, we have

$$-r_{TPH} = -\frac{dC_{TPH}}{dt} = k_d C_{TPH} \tag{11}$$

Where;

Q_o = Inlet volumetric flow rate (kg/day)

Q = Outlet volumetric flow rate (kg/day)

$C_{TPH(o)}$ = Initial concentration of Pollutant (TPH) (mg/kg)

C_{TPH} = Instantaneous concentration of Pollutant (TPH) (mg/kg)

V = Volume of reactor (m^3)

r_{TPH} = Rate of TPH degradation (mg/kg.day)

k_d = TPH degradation rate constant (day^{-1})

t = Time of TPH degradation (day)

Integration of equation (11) by the separation of variable method yields the following

$$\int_{C_{TPH(o)}}^{C_{TPH(t)}} \frac{dC_{TPH}}{C_{TPH}} = -k_d \int_0^t dt \tag{12}$$

$$\ln\left(\frac{C_{TPH(t)}}{C_{TPH(o)}}\right) = -k_d t \tag{13}$$

$$\ln C_{TPH(t)} - \ln C_{TPH(o)} = -k_d t$$

$$\ln C_{TPH(t)} = \ln C_{TPH(o)} - k_d t \tag{14}$$

Equation (14) can be simply written as

$$\ln C_{(t)} = \ln C_o - k_d t \tag{15}$$

Equation (15) can be compared with the general linear equation of the form

$$y = mx + C \tag{16}$$

where;

$y = \ln C_{(t)}$

$x = t$

$m = k_d$

$C = \ln C_o$

A plot of $\ln C_{(t)}$ against t, gives a linear (straight line) graph with slope equivalent to "k_d" and intercept equivalent to $\ln C_o$.

However, to obtain the instantaneous TPH concentration, exponential of both sides of equation (15) is taken to give

$$C_{TPH(t)} = C_{TPH(o)} \exp(-k_1 t) \tag{17}$$

Equation (17) is the predictive first order kinetic model for TPH reduction during the treatment process.

The Second Order Biodegradation Rate Kinetic Model

The degradation rate of TPH would be further tested with the second order rate kinetics and it is expressed as:

$$-r_{TPH} = -\frac{dC}{dt} = k_d C^2 \tag{18}$$

Upon integration of equation (18), we have as follows.

$$\int_{C_o}^{C_t} C^{-2} dC = -\int_0^t k_d dt$$

$$\frac{1}{C_t} - \frac{1}{C_0} = k_d t \tag{19}$$

Or

$$\frac{1}{C_t} = \frac{1}{C_0} + k_d t \tag{20}$$

Where;

C_0 and C_t are the initial and concentration of TPH at any time, *t*; while k_d is the degradation rate constant for the second order.

A plot of $\frac{1}{C_t}$ against t will give slope as k_d and $\frac{1}{C_0}$ as intercept.

Rearranging equation (20) with little manipulations gives the TPH predictive equation using the second order kinetic model as:

$$C_{TPH(t)} = \frac{C_{TPH(0)t}}{1 + C_{TPH(0)} k_2 t} \tag{21}$$

3. RESULT AND DISCUSSION

Evaluation of Treatment Performance in TPH Removal from Soil

The performances of moringa seed shell and elephant grass in powdered form, yeast and NPK in swampy soil in terms of the removal of TPH from polluted swampy soil and clay soils are evaluated (Figures 2, 3, 4). While the effectiveness of the treatments in the respective soil was evaluated with respect to time at only 100g weight of treatment. According to Figure 2, the performances of the two treatments were compared for each soil with respective to weight at only the 84th day of the analysis (Figures 3, 4).

Figure 2 shows the TPH percentage degradation in swampy soil and clay soils obtained at 100g weight of moringa seed shell and lephant Grass treatments with time. The percentage of TPH removed from the soils actually increased with time, but the removing rate varies for each treatment. The percentage of TPH removed increased from 0% to 97.78%, 97.38%, 98.50% and 97.69% for moringa seed shell (SCM), moringa seed shell in clay soil (CM), Elephant Grass in Swampy Soil (SCEG) and Elephant Grass in clay soil (CEG) respectively at the 84th day. However, within the first 42 days, the order of the degradation effciency are CM>CEG>CSM>CEG, but beyond this period, SCEG performance then slightly edged the others, while the CM which recorded the highest performanmce within the first 42 days became the least.

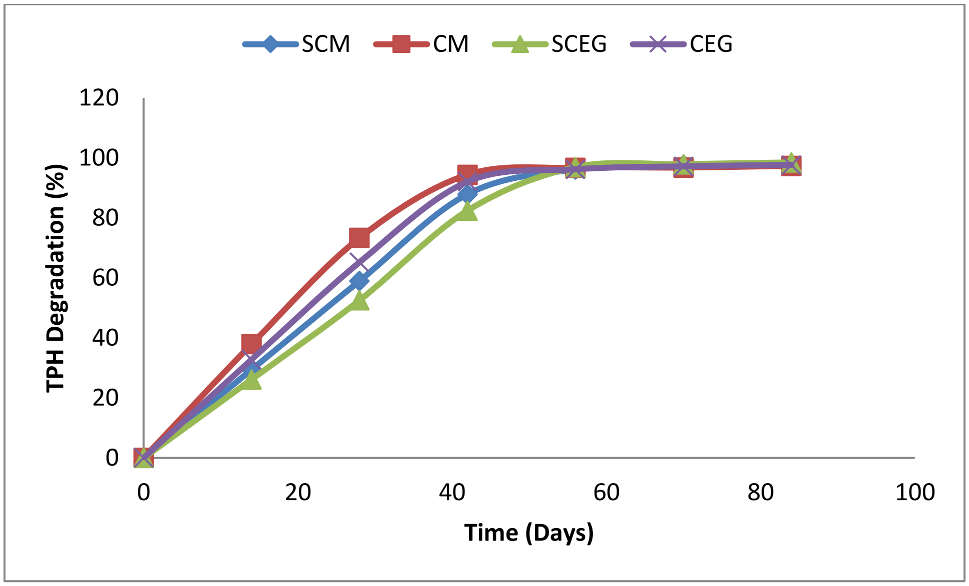

Figure 2 Performance of Treatments in Swampy Soil and Clay Soils after 84 Days

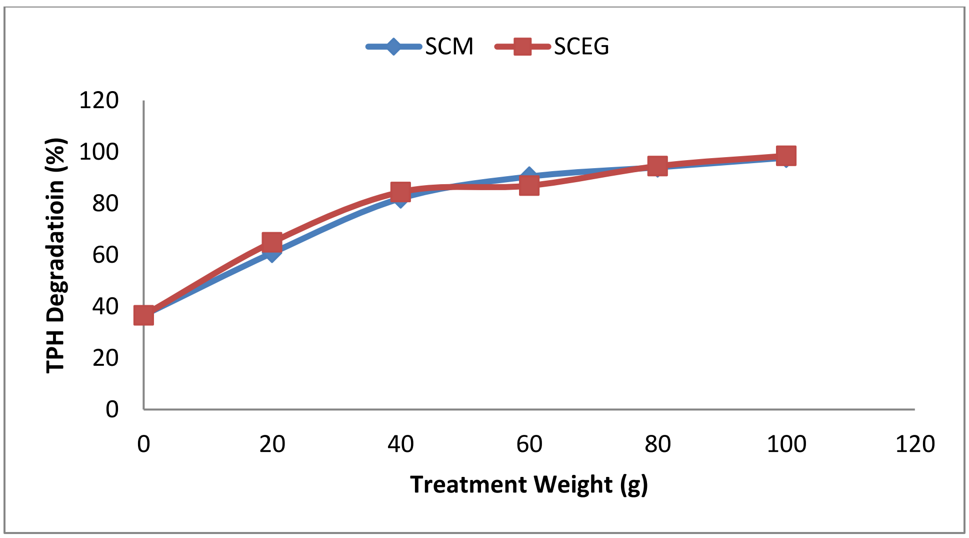

Figure 3 Comparison of TPH Degradation with CSM and CSEG

Figure 3 demonstrates the TPH degradation percentage at varying treatment weights in swampy soil. This study revealed that TPH degradation percentage increases as treatment weight was increased. However, at the 84th day of the investigation, elephant grass in powdered form, yeast and NPK in swampy soil treatment slightly edged the moringa seed shell in powdered form, yeast and NPK in swampy soil treatment in silty clay, though, not significant as depicted. The comparison of the moringa seed shell in powdered form, yeast and NPK in swampy soil and elephant grass in powdered form, yeast and NPK in swampy soil treatments in swampy soil. However, from the analysis, the TPH degradation percentage in swampy soil at 20g to 100g treatment weight increased from 60.79% to 97.78% with moringa seed shell in powdered form, yeast and NPK in swampy soil and 64.95% to 98.50% with elephant grass in powdered form, yeast and NPK in swampy soil.

Figure 4 illustrates the TPH degradation percentage at varying treatment weights in clay soil. Again, it was revealed that TPH degradation percentage increased as treatment weight was increased in clay soil, while the elephant grass in powdered form, yeast and NPK in swampy soil treatment slightly edged the moringa seed shell in powdered form, yeast and NPK in swampy soil treatment. The comparison of the moringa seed shell in powdered form, yeast and NPK in swampy soil and elephant grass in powdered form, yeast and NPK in swampy soil treatments in clay soil. Therefore, from the analysis, the TPH degradation percentage in clay soil at 20g to 100g weight of treatment increased from 66.89% to 97.38% with moringa seed shell in powdered form, Yeast and NPK in swampy soil and 69.74% to 97.69% with elephant grass in powdered form, yeast and NPK in swampy soil.

This scenario was observed almost in all the treatment options, although, both treatments proved to be effective for bioremediation of Total Petroleum Hydrocarbons content from polluted soil.

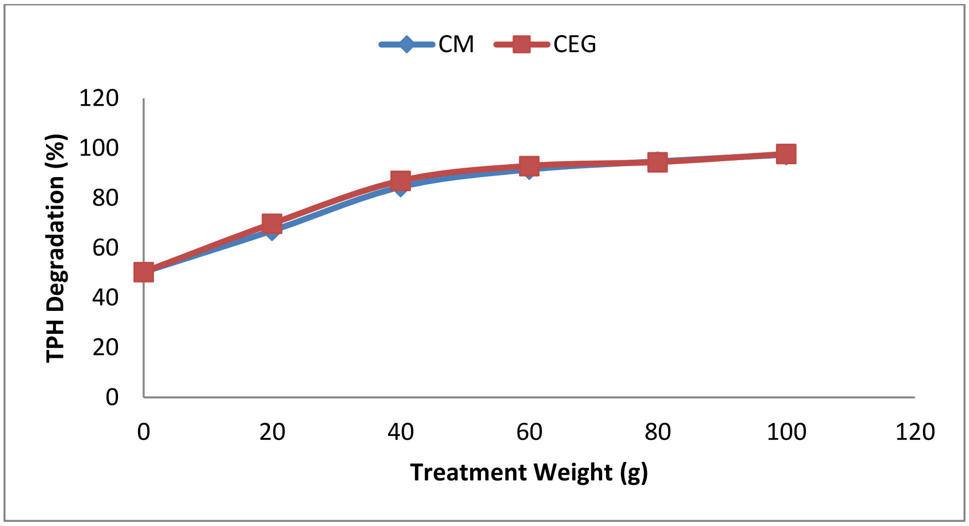

Figure 4 Comparison of TPH Degradation with CM and CEG

Degradation Rate Constant for Model Prediction of TPH in Soil

The degradation of TPH in soil environment has been extensively studied via kinetic models, which has been a useful tool for understanding of the reaction dynamics of crude oil during bioremediation (Talha et al., 2018; Tekere, 2019). In literature, the first order degradation rate kinetics has been the most applied model for prediction of TPH with time. However, in addition to the first order rate model, the second order rate and the Micaelis-Menten models were used in this study. This is to compare the predictability of the models and suggest which model best suited the study of TPH degradation in soil amended with moringa seed shell in powdered form, yeast and NPK in swampy soil and elephant grass in powdered form, yeast and NPK in swampy soil. To effectively utilize these models as expressed the kinetic parameters must be first determined (Ukpaka and Nkakina, 2017).

First Order Degradation Rate

The degradation rate constant in the first order rate kinetic model was determined by using equation 4. The plots as in Figure 5, 6, 7 and 8 illustrates the first order rate kinetics of swampy soil treated with only powder form of moringa seed shell in powdered form, yeast and NPK in swampy soil for various reactors conditions of 20g, 40g, 60g, 80g and 100g. The rate values where determined based on mass of moringa seed shell in powdered form, yeast and NPK in swampy soil powder form, yeast and NPK introduced in each reactor.

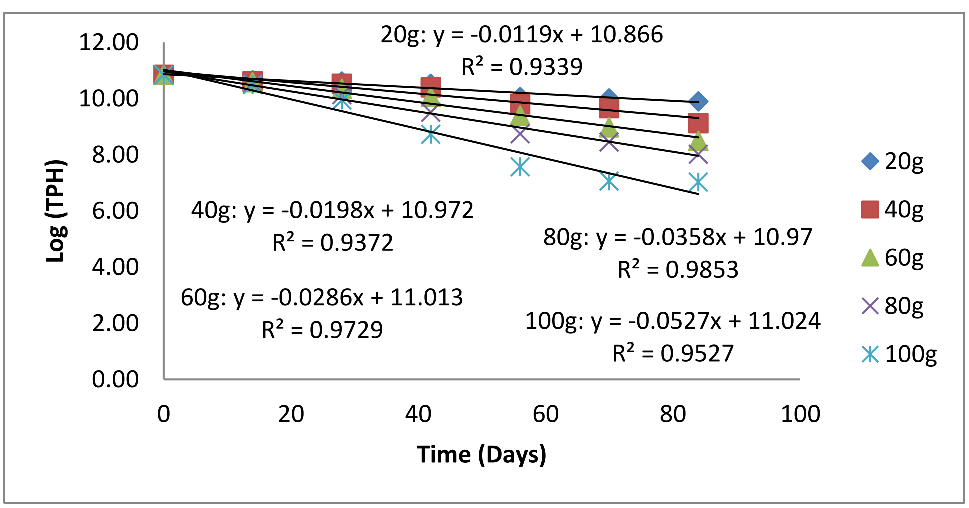

Figure 5 Graph of Log (TPH) in Swampy Soil against Time for Mixture of Moringa Seed Shell in Powdered Form, Yeast and NPK

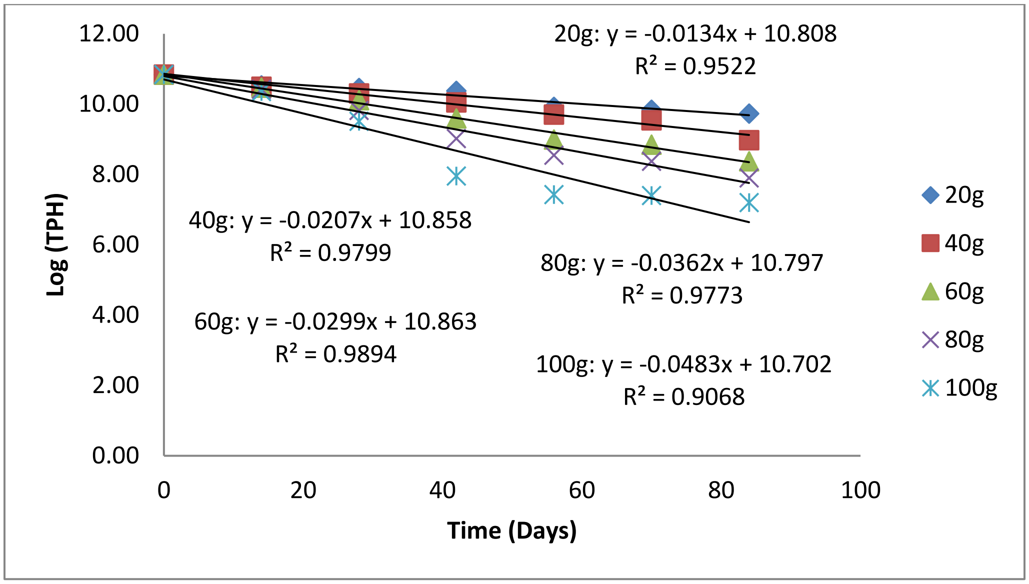

Figure 6 Graph of Log (TPH) in Clay Soil against Time for Mixture of Moringa Seed Shell in Powdered Form, Yeast and NPK

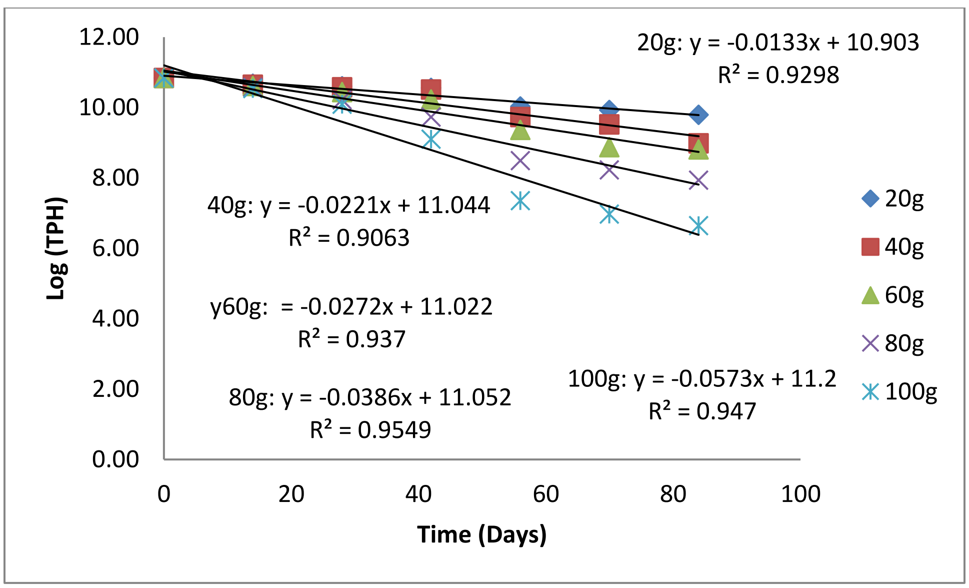

Figure 7 Graph of Log (TPH) in Swampy Soil against Time for Mixture of Elephant Grass in Powdered Form, Yeast and NPK

Figures 5, 6, 7 and 8 were used to calculate the degradation rate constant, *k* for the first order rate kinetic model. Thus, from the given equations on the plots and comparing with equation 14 the respective predictive model can be obtained for each of treatment in the soils. For instance, the respective predictive model determined from the first order rate model for Swampy Soil treated with moringa seed shell in powdered form, yeast and NPK in swampy soil (Table 1). For instance, the predictive model for residual TPHs in swampy soil treated with moringa seed shell in powdered form, yeast and NPK in swampy soil at the different treatment options is presented (Table 1). The degradation rate constant (*k*) for the respective treatment options (Table 1), which has been inserted in the original model.

From Table 1, it was observed that the degradation rate constant, *k* increased with increase in the weight of moringa seed shell in powdered form, yeast and NPK in swampy soil treatment. The variable *x* in the regression equation stands for time, while the coefficient of *x* is the TPH degradation constant *k*. The negative sign in the equation indicates that TPH is reduced with time, and $R^2$is the correlation coefficient, which shows the degree of agreement between the experimental value and the predicted counterpart. Also, the degradation rate constant, *k* reported in previous works for first order rate model (Table 2). Hence, the TPH degradation constant *k* obtained in this study are within the reported values in previous works.

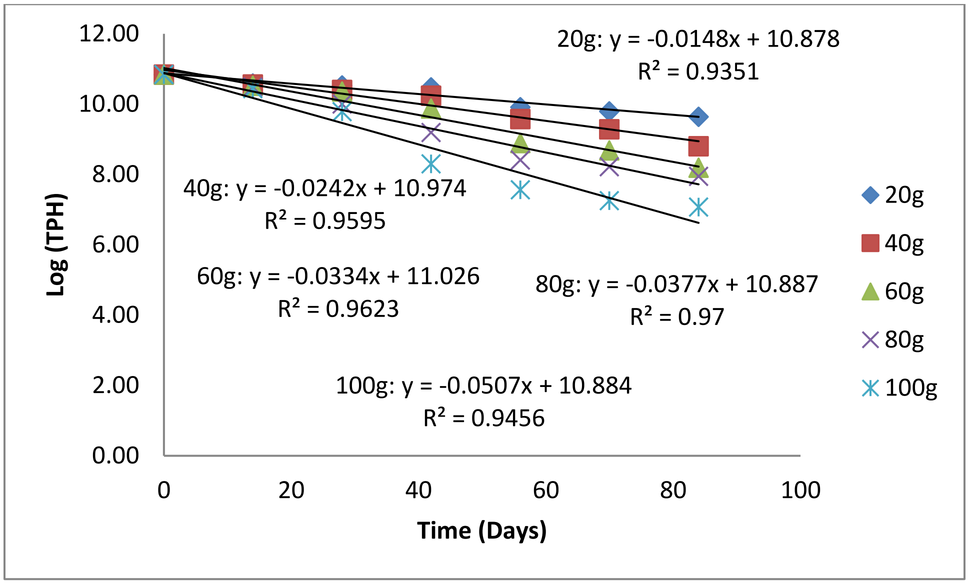

Figure 8 Graph of Log (TPH) in Clay Soil against Time for Mixture of Elephant Grass in Powdered Form, Yeast and NPK

Table 1 Degradation Constant and First Order Rate Model

Weight (g)	Regression Equation	K (day^{-1})	Predictive Model
20	$\ln C_{TPH} = -0.0119t + 10.866$	0.0119	$C_{TPH} = 51067.73e^{-0.00119t}$
40	$\ln C_{TPH} = -0.0198t + 10.972$	0.0198	$C_{TPH} = 51067.73e^{-0.00198t}$
60	$\ln C_{TPH} = -0.0286t + 11.013$	0.0286	$C_{TPH} = 51067.73e^{-0.00286t}$
80	$\ln C_{TPH} = -0.0358t + 10.970$	0.0358	$C_{TPH} = 51067.73e^{-0.00358t}$
100	$\ln C_{TPH} = -0.0527t + 11.024$	0.0527	$C_{TPH} = 51067.73e^{-0.00527t}$

Table 2 Reported TPH Degradation Rate Constant (k_d) for different Treatments

Treatment	k_d (day^{-1})	Reference
Beans Shell	0.0251	-
Cassava Peel	0.0288	-
Cow Dung	0.0498	-
Groundnut Shell	0.0260	-
Melon Shell	0.0257	-
NPK Fertilizer	0.0228	-
Pig Dung	0.0266	-
Cow Dung	0.016	
NPK Fertilizer	0.025	-
Poultry Manure	0.017	-
Compost	0.0352	
Spent Mushroom	0.0366-0.0386	
20g treatment	0.0119-0.0148	This Work
40g treatment	0.0198-0.0242	This Work
60g treatment	0.0272-0.0334	This Work
80g treatment	0.0358-0.0386	This Work
100g treatment	0.0483-0.0573	This Work

Second Order Degradation Rate

The degradation rate constant for the second order rate kinetic model was determined using equation (19) upon obtaining the plots (Figure 9, 10, 11, 12), the regression equations were then used to evaluate the rate constant for the different weights investigated in the study.

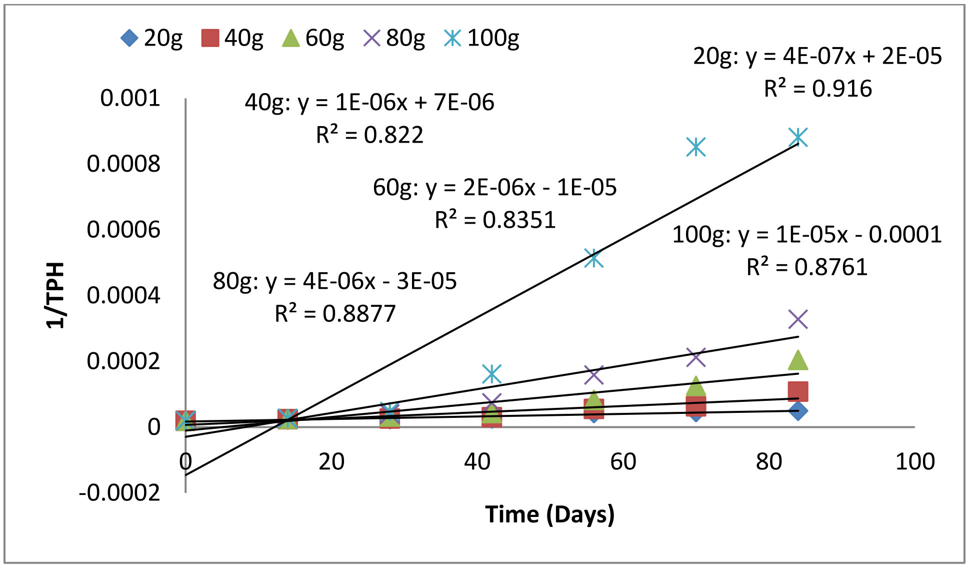

Figure 9 Reciprocal of $^1/_{TPH}$ in Swampy Soil against Time for Mixture of Moringa Seed Shell in Powdered Form, Yeast and NPK

Figure 9, 10, 11 and 12 show the plots for calculation of TPH degradation rate constant, *k* for the second order rate kinetic model, which were obtained using with equation (19). Again, from the regression equations on the plots, the second order TPH degradation rate constants were evaluated for the different weights of treatments.

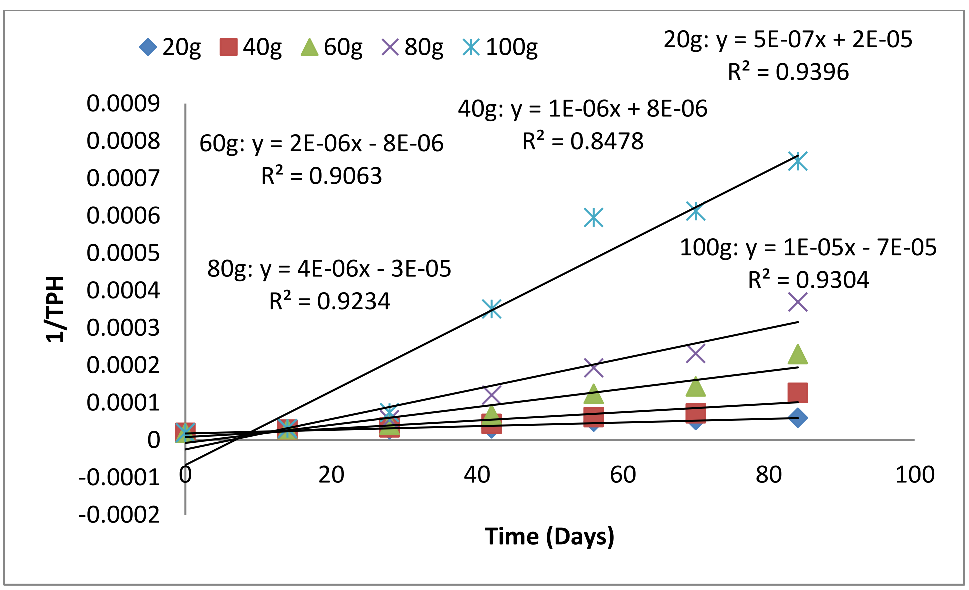

Figure 10 Reciprocal of $^1/_{TPH}$in Clay Soil against Time for Mixture of Elephant Grass in Powdered Form, Yeast and NPK

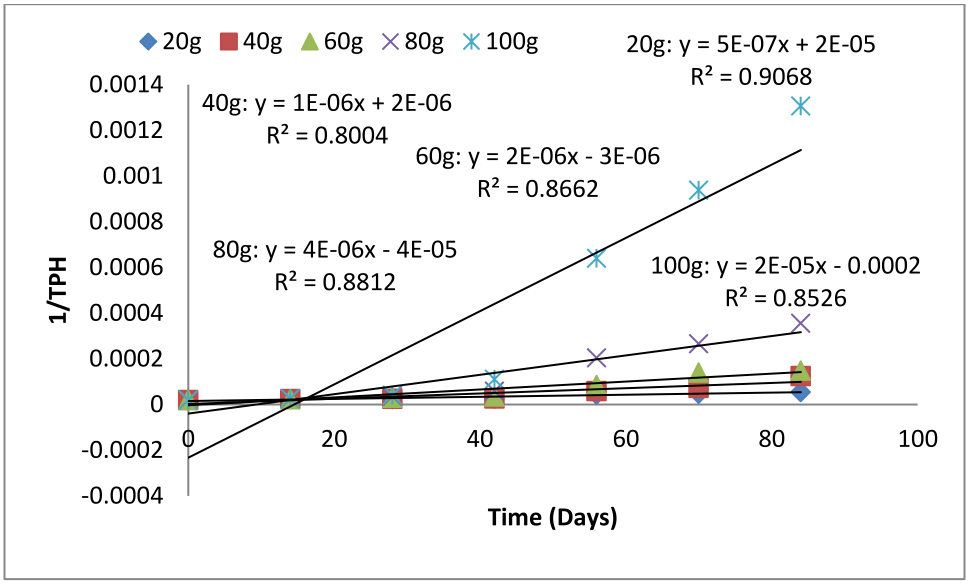

Figure 11 Reciporical of $^1/_{TPH}$in Swampy Soil against Time for Mixture of Elephant Grass in Powdered Form, Yeast and NPK

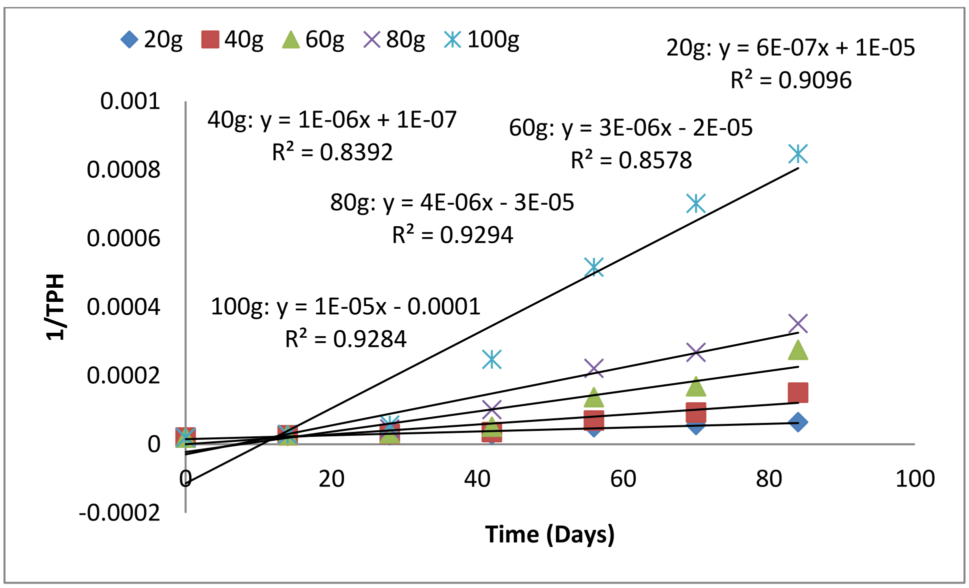

Figure 12 Reciporical of $^1/_{TPH}$in Clay Soil against Time for Mixture of Elephant Grass in Powdered Form, Yeast and NPK

Table 3 TPH Degradation Predictive Model using the Second Order Rate Model

Weight (g)	Predictive Model
20	$C_{TPH} = \frac{51067.73}{1+0.0204t}$
40	$C_{TPH} = \frac{51067.73}{1+0.0511t}$
60	$C_{TPH} = \frac{51067.73}{1+0.1021t}$
80	$C_{TPH} = \frac{51067.73}{1+0.2043t}$
100	$C_{TPH} = \frac{51067.73}{1+0.5107t}$

The coefficient of time, *t* in the respective equations (Table 3) is the products of the initial TPH concentration and the second order degradation rate constant. The time coefficient increases with increase in the weight of treatment.

4. CONCLUSION

The elephant grass treatment slightly edged the moringa seed shell in terms of TPH removal from both soils. This is justified by the higher content of total nitrogen and phosphorus in soils amended with elephant grass, which supplied more nutrients to the hydrocarbon degrading bacteria. However, both treatments showed high promise for TPH remediation in polluted soils. The results obtained from the predictive models, the degree of TPH degradation prediction between the Michalis-Menten rate model and the first order degradation rate model cannot be easily distinguished, performed better than the second order kinetic rate.

Informed consent
Not applicable.

Ethical approval
Not applicable.

Conflicts of interests
The authors declare that there are no conflicts of interests.

Funding
The study has not received any external funding.

Data and materials availability
All data associated with this study are present in the paper.

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